

X-Ray Absorption Spectroscopy of Liquid and Gaseous Water

K. R. Wilson [a], R. J. Saykally [a], and J. G. Tobin [b];

a: Dept of Chemistry, University of California, Berkeley, California 94720

b: Lawrence Livermore National Laboratory, Livermore, California 94550

X-ray absorption fine structure (XAFS) measurements have been performed upon liquid [1] and gaseous [2] H₂O. Using the O1s level as the means of achieving elemental specificity, both near edge (NEXAFS) and extended X-ray absorption fine structure (EXAFS) have been measured. Liquid water samples were achieved in the vacuum system via the utilization of a liquid jet system modelled after that of Faubel et al. [3]. In fact, the liquid jet system permitted the probing of the liquid water by synchrotron radiation (SR) without the inclusion of any windows or other such isolation devices, while maintaining the UHV nature of the SR beamline and SR source. In the investigation of liquid water, both ions and electrons were used as a means of detection. This permitted the separation of liquid surface effects (ions) from bulk-like behavior (electrons). In the NEXAFS regime, the surface sensitive spectrum resembled that of gaseous water while the bulk-sensitive spectrum exhibited broadening and a blue shift. Similarly, differences were observed in the EXAFS results derived from each detection method, i.e. surface vs. bulk. The measurement of the EXAFS in liquid water encouraged us to go back and perform similar measurements upon gaseous water. Interestingly, it was possible to observe the effects of scattering of the excited O1s electrons off of the nearby hydrogen atoms, an event deemed impossible by conventional wisdom. A single oscillation was observed from gaseous water consistent with the location of the covalently bonded hydrogen in H₂O. The experimental phase and amplitude of the oscillation are in excellent agreement with curved wave multiple scattering calculations for isolated water molecules, performed by Ankudinov and Rehr [2]. With this determination of the O-H scattering phase shift, the covalent hydrogen bond distance (0.95 ± 0.03 Å) in liquid water has been quantified, thus demonstrating that hydrogen EXAFS can become a valuable complement to existing structural methods in chemistry and biology.

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3. M. Faubel et al, J.Chem. Phys. 106, 9013 (1997).

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Corresponding Author: JG Tobin, LLNL, 7000 East Ave., POB 808, L-357 Livermore, CA, USA, 94550:
Tel 925-422-7247; Fax 925-423-7040, Email Tobin1@LLNL.Gov